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Presented at Arctic and Marine Oilspill Program, June 10-12, 2003, Vancouver, BC, Canada

Field Instruments for Real Time In-Situ Crude Oil Concentration Measurements

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Abstract
In this paper, we describe five sensors for rapid monitoring of crude oil concentrations in an aquatic system. These measurements are critical for monitoring plume transport as well as for estimating PAH exposure concentrations for toxicity risk assessments. A submersible multi-angle laser scattering instrument (LISST-100, Sequoia Instruments), an ex-situ single wavelength fluorometer (AU-10 field fluorometer, Turner Designs), an in-situ single wavelength fluorometer (Flashlamp, WET Labs), and two in-situ multiple wavelength fluorometers (ECO-FL3 and SAFire, WET Labs) are evaluated for sensitivity and bias. For each instrument, a brief discussion of its operating principles is presented. Crude oil emulsions of various concentrations were analyzed using the above instruments. The implications of potential interferences and instrument limits are discussed relative to their importance for real time monitoring of crude oil spills.

1.0 Introduction
Technological advances have led to the evolution of oil spill monitoring instrumentation. The simplest is basic aerial visual monitoring, in which trained observers photograph the oil and dispersant cloud, estimate actual dispersion, reappearance of sheen, and the overall effectiveness of applying dispersants toward meeting the goals of the dispersant application.

More sophisticated monitoring can be conducted using a variety of analytical instrumentation coupled with the actual collection of dispersed oil samples throughout the treatment areas at specified depths of the water column. Traditionally, single wavelength fluorometry has been used in monitoring the dispersion of a spilled crude oil slick. The fluorescence principle is based on the ability of a compound (aromatic hydrocarbons) to be subjected to a specific wavelength of light (excitation) and to re-emit this light at one, or more, higher wavelengths (emission). The wavelengths are registered as peaks. The measured fluorescence is a direct indicator of the hydrocarbon concentration. The aromatic hydrocarbon concentration is used as a proportional indicator of total hydrocarbons, which is then displayed in ppm.

Light scattering instrumentation provides an alternate means to monitor crude oil dispersion. Nearly all of the dispersed oil volume exists in the water column as entrained droplets. A laser beam formed by collimating the output of a diode laser illuminates the droplets. Scattering by droplets is detected in the focal plane of a receiving lens. Mie theory is used to estimate the droplet size distribution.

While the variety of instruments have increased, the effectiveness of each type of instrument in quantitative oil spill monitoring remains unclear. This work compares the response of a suite of commercial fluorometers and a particle-sizing instrument to a range of dispersed oil loadings. We present response curves for each instrument to a chemically dispersed crude oil in filtered, synthetic seawater. Additionally, we discuss potential advantages and limitations of each instrument for oil spill monitoring.

2.0 Experimental Methods

2.1 Apparatus. The reactor configuration used for this experiment was a derivative of the standard jar test apparatus. As with the jar test apparatus, this reactor system was agitated using a stainless steel mixing impeller. A number of instruments were used for oil concentration monitoring (Table 1). An in-situ laser scattering particle sizer (LISST-100, Sequoia Instruments, Richmond, WA) was installed through one end wall of the reactor. In-situ fluorometers (ECO-FL3 and Flashlamp, WET Labs, Philomath, OR) were suspended directly in the reactor. Continuous flow analysis was conducted using ex-situ fluorometers (SAFire, WET Labs, Philomath, OR and 10-AU Field Fluorometer, Turner Designs). An electric pump was attached to the fluorometers so that water from the reactor was pulled through the polyethylene tubing, SAFire, 10-AU fluorometer, pump, and back to the reactor.

2.2 Concentration Measurements. The reactor described above was filled with fifty liters of synthetic sea water (Instant Ocean, Aquarium System, Mentor, OH). The reactor salinity was verified using a DataSonde (HydroLab, Loveland, CO). A dispersed oil solution containing 10 ml of weathered Medium Arabian crude oil and 1 ml of Corexit® 9500 was homogenized. One ml of this mixture was diluted to 1 L using synthetic seawater and mixed by inverting the volumetric flask. This diluted solution served as the stock solution to be added to the reactor for concentration measurements. For this series of experiments, nominal oil concentrations were 10, 100, 250, 500, 750, 1000, 5000, and 10000 ppb.

Using a wide tipped pipette, a nominal volume of the stock oil-dispersant mixture was injected near the rotating impeller shaft. For a five-minute measurement period, a series of dynamic droplet size distributions were measured using an in-situ laser scattering particle sizer (LISST-100) and analyzed using instrument software. Raw count data from the Flashlamp and the ECO-FL3 were captured using Windows Hyperterminal software. Raw count data from the 10-AU Field Fluorometer were hand recorded from the instrument display window. Raw count data from the SAFire were captured using instrument software.

3.0 RESULTS

3.1 Sequoia LISST-100

The LISST-100 utilizes a specially constructed detector consisting of 32 log-spaced rings for detecting light scatter for particle size analysis. The detector also has a center hole, which allows passage of the strong direct beam for transmissometry measurements. Figure 1a and b illustrate response data for the LISST-100. Total volume concentration in figure 1b is the sum of the volume concentrations in each of the 32 size bins.

Over the measured range, both data sets are linear ($r^2 > 0.999$). Similarly, the reproducibility of the curve is high as there is only a 5% difference in the response measured on the two days. For concentrations less than 100 ppb, data noise is greater than the measurement. This is due to the high transmissivity of the water. Because the LISST-100 has an instrument specific calibration based on optical parameters, it does not require a specific chemical or oil calibration for absolute volume quantification. However, the presence of bubbles or suspended sediment will impair accurate oil quantification as these also produce significant light scatter.

3.2 WET Labs Flashlamp

The Flashlamp uses a single wavelength light to monitor crude oil concentrations. The sample is exposed to 230 nm light while an emission filter in front of the photodetector allows fluorescence at 350 nm to register. Figure 2 shows the response of the Flashlamp to measured crude oil concentrations. For both days, the response was linear ($r^2 > 0.98$) and consistent, as the slope values agree within 10%. For the entire measured range, the response values were greater than the noise. This suggests that the Flashlamp can detect changes in oil concentration throughout the measured range. Calibration with the oil is required to related fluorescence counts to oil concentration (ppb). However, this instrument is less susceptible to physical interferences such as bubbles or suspended sediments.

3.3 Turner Designs 10-AU Field Fluorometer

The Turner Designs 10-AU Field Fluorometer was configured with the 25 mm one-piece flow cell. Turner Designs provides two sets of lens for monitoring oils. For long wavelength oils, the sample is exposed to 300-400 nm light while an emission filter in front of the photodetector allows only fluorescence at 500 nm +/- 100 nm to register. For short wavelength oils, the sample is excited with 254 nm light while fluorescence at 350 +/- 50 nm is monitored. The long wavelength lenses were used for consistency with that of the Coast Guard SMART protocol. A three-point calibration of the instrument was performed using fluorescein dye. The Auto Ranging feature was enabled to most accurately estimate oil concentrations.

Figure 3 shows the response of the 10-AU Field Fluorometer to measured crude oil concentrations. For both days, the response was linear ($r^2 > 0.999$). However, the response values were slightly less consistent compared with the previous instruments, having a difference of approximately 15%. In addition, at 15,000 and 20,000 ppb, the concentrations were above the measurement range of the 10-AU Field Fluorometer. As with the WET Labs Flashlamp, calibration with the oil is required to relate fluorescence counts to oil concentration (ppb).

3.4 WET Labs ECO-FL3

The WETLabs ECO-FL3 is a newly developed, in-situ, multiple wavelength fluorometer. Excitation wavelengths are 390 and 470 nm while emission wavelengths are 460, 530, and 695 nm. Response curves are shown for the chlorophyll A (EX 470 nm/EM 695 nm) and CDOM (EX 390 nm/EM 460 nm) wavelengths (Figure 4). The most significant response was noted on the chlorophyll A wavelength (nm), while only minimal responses were observed on the CDOM or fluorescein (nm) wavelengths. The chlorophyll A response was linear ($r^2 > 0.99$) with response reproducibility similar to that of the Turner 10-AU Field Fluorometer (within 15%). However, the data noise at concentrations less than 1000 ppb was greater than the mean response values. This suggests that the ECO-FL3 would have problems quantitatively detecting changes in oil concentration below this threshold value. As with the previous fluorometers, calibration with the crude oil is required to relate fluorescence counts to oil concentration (ppb).

3.5 WET Labs SAFire

The WETLabs SAFire is a multi-spectral fluorometer. Excitation wavelengths are 228, 265, 313, 340, 430, and 437 nm while emission wavelengths are 228, 265, 313, 340, 375, 400, 430, 460, 490, 540, 565, 590, 620, 650, 685, and 810 nm. This results in 96 measured excitation/emission fluorescence pairs. For this study, the 228 nm excitation/340 nm emission response and the 340 nm excitation/460 nm emission response are highlighted (Figure 5a and b). For the 228 excitation/340 emission pair (Figure 5a), the response was linear ($r^2>0.98$) and consistent. The instrument response slope values were within 5% of each other. For the entire measured range, the mean response was greater than the measurement noise. For the 340 excitation/460 emission pair (Figure 5b), the response was less linear ($r^2 > 0.92$) and less consistent. The slope values are within 30% of each other. This suggests that the 228 nm excitation/340 nm emission on the SAFire can detect changes in oil concentration throughout the measured range. As with the previous fluorometers, calibration with the crude oil is required to relate fluorescence counts to oil concentration (ppb).

4.0 CONCLUSIONS

The following conclusions can be made from this study:

1. All of the instruments tested followed a linear response ($r^2>0.98$) within the tested concentration range (10-20000 ppb).
2. At the lowest concentrations, the LISST-100 was not as effective as the flourometers due to the limited particle volume present for scatter.
3. For Turner Designs AU-10 Field Fluorometer, the highest concentrations tested were above the measurement range of the instrument.

5.0 ACKNOWLEDGEMENTS

We would like to acknowledge the Texas General Land Office (Robin Jamail) for supporting this project.

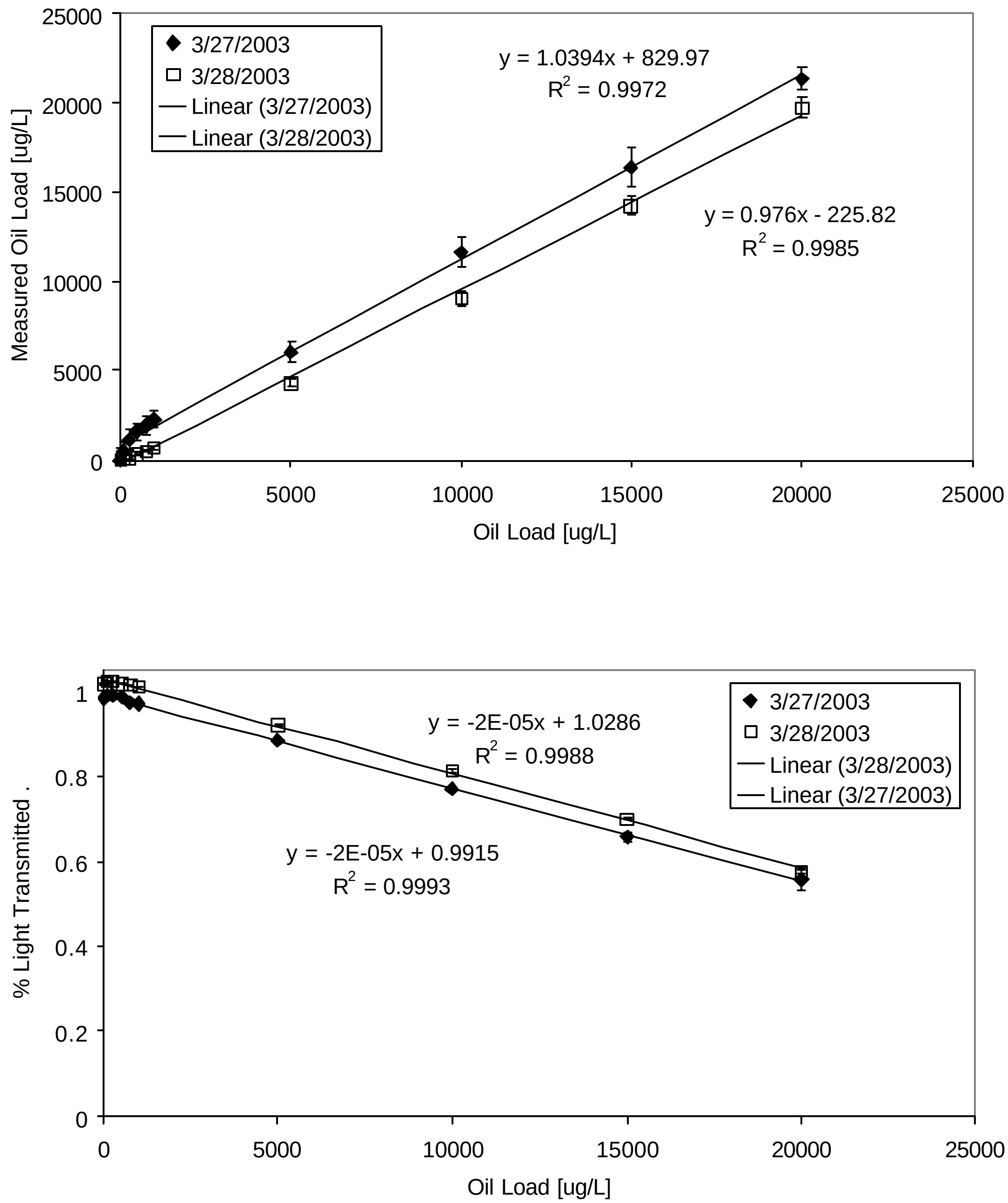

Figure 1. LISST-100 particle sizing (a) and transmissometry (b) response data for chemically dispersed crude oil in saline water.

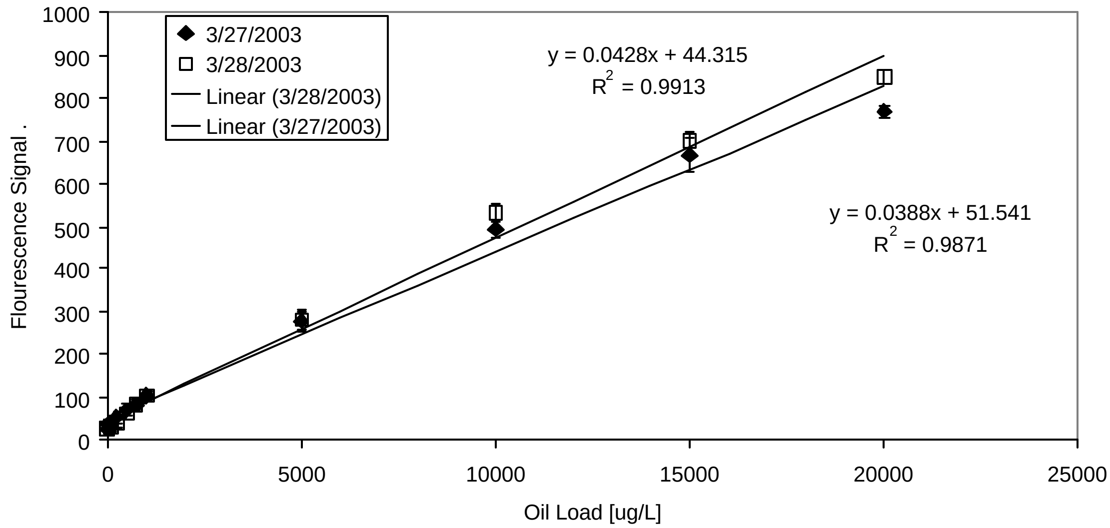

Figure 2. WETLabs Flashlamp fluorescence response data for chemically dispersed crude oil in saline water.

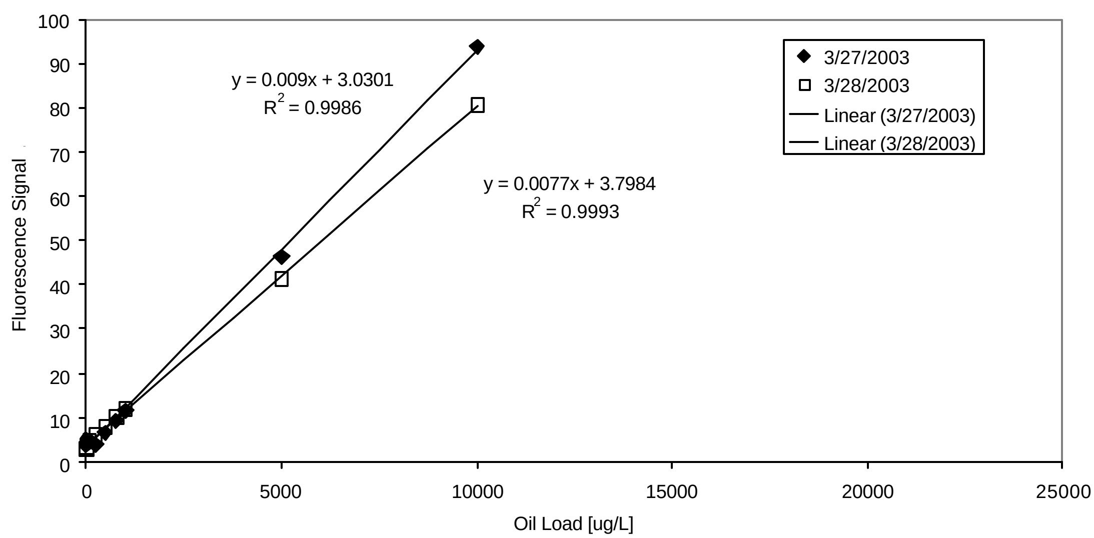

Figure 3. Turner Designs AU-10 Field Fluorometer fluorescence response data for chemically dispersed crude oil in saline water.

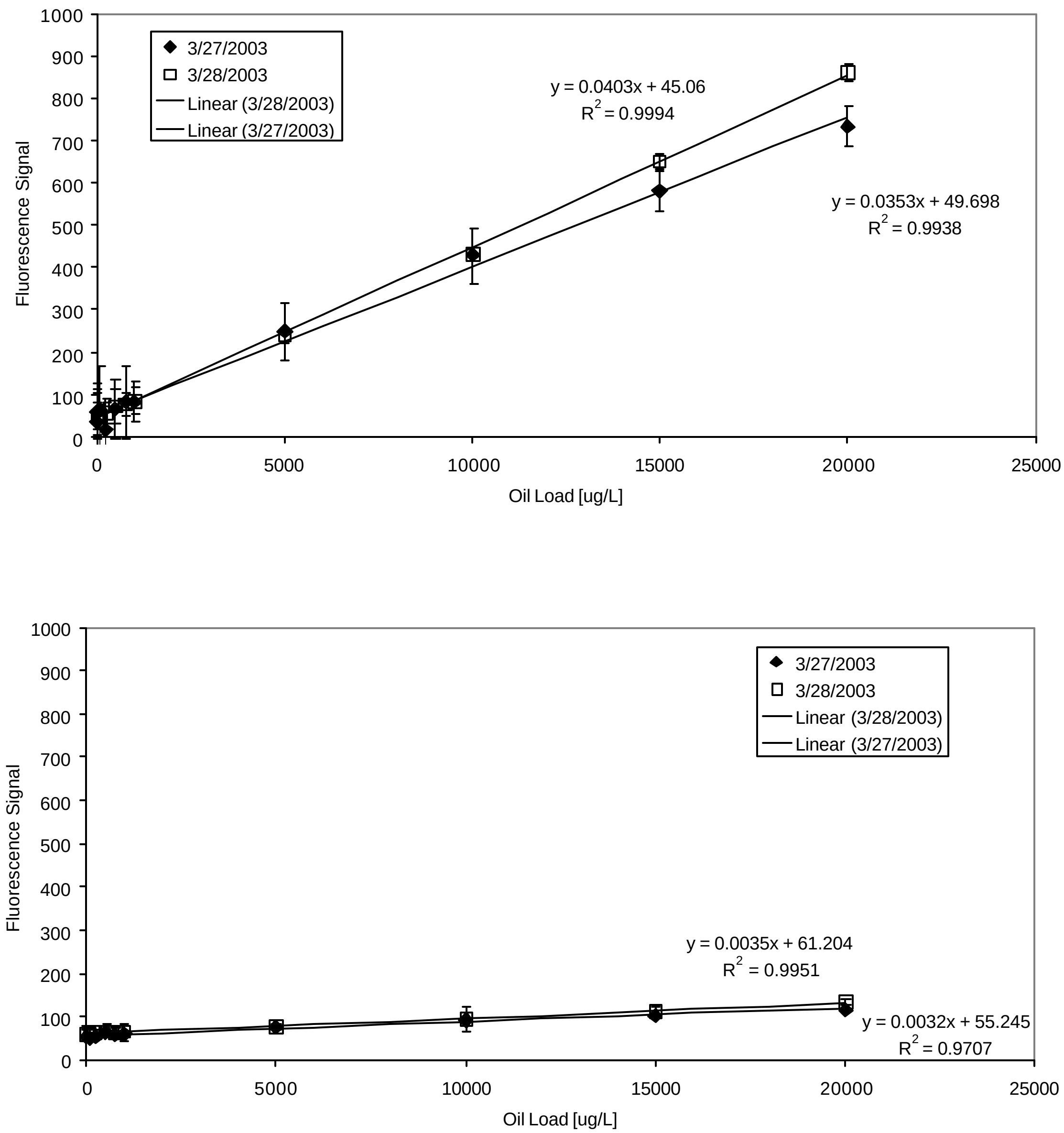

Figure 4. ECO-FL3 fluorescence response data for chemically dispersed crude oil in saline water. (a) 470 nm ex/695 nm em, (b) 390 nm ex/460 nm em.

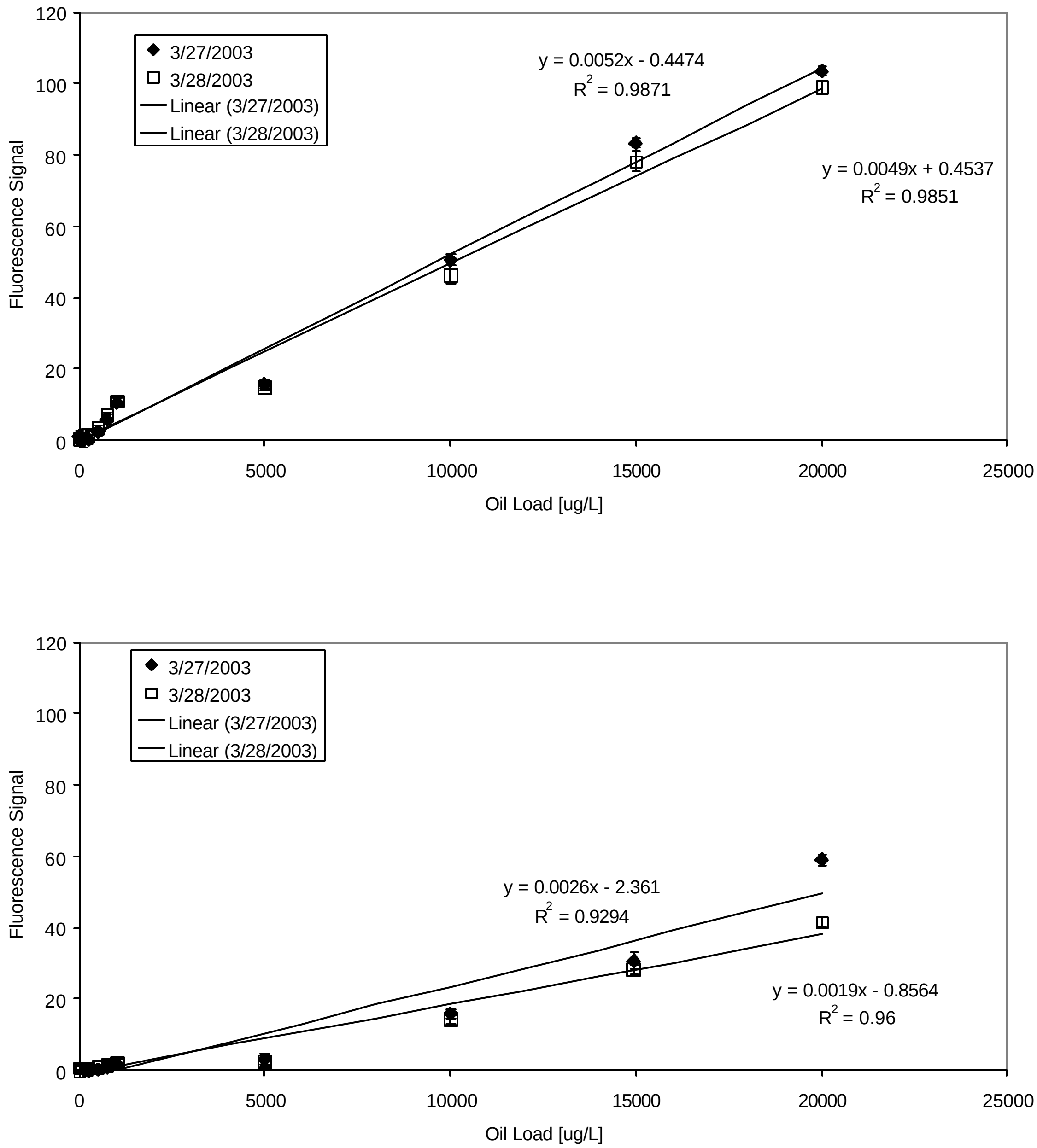

Figure 5. SAFire fluorescence response for chemically dispersed crude oil in saline water. (a) EX 228 nm/EM 340 nm, (b) EX 340 nm/EM 460 nm.